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Published in:
Journal of Physics and Chemistry of Solids

DOI:
10.1016/S0022-3697(97)00097-8

Publication date:
1997

Pergamon PII: S0022-3697(97)00097-8

J. Phys. Chem Solids Vol 58, No. 11, pp. 1983-1990, 1997

0022-3697/97 $17.00 + 0.00

NEW DEVELOPMENTS IN THE ORGANIC CHEMISTRY OF FULLERENES

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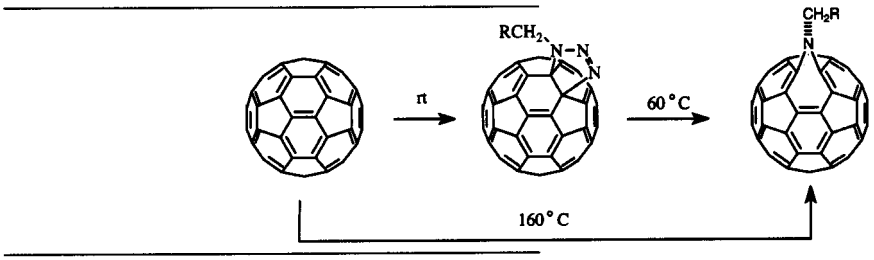
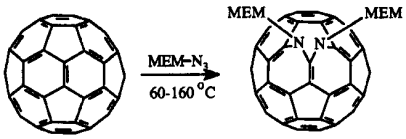
Since the discovery and isolation of macroscopic quantities of the fullerenes, the preparation of derivatives has grown rapidly over the last few years [1-3]. Functionalization of C_{60} in our group has been done primarily by cycloaddition reactions; particularly the 1,3-dipolar addition of diazoalkanes and alkyl azides.



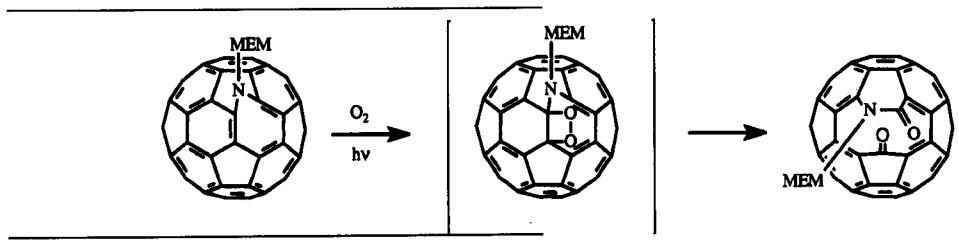
Unlike the addition of a second equivalent of diazoalkane to C_{60}, which does not show marked selectivity, the addition of azides to C_{60} shows chemo and regio selectivity [4]. Utilization of this unique selectivity, led us to the preparation of the first heterofullerene '$C_{59}N$' in bulk quantity [5, 6]. Herein we report on its synthesis and mechanism of formation. We also describe the application of this procedure for the formation of higher heterofullerene analogs, i.e. '$C_{69}N$' isomers [7] and introduce methodology that opens a viable route to the functionalization of azafullerenes [8].

The azafullerene $(C_{59}N)_2$ can be synthesized from C_{60} in three steps. The initial step in the formation of azafullerenes is the 1,3-dipolar cycloaddition of 2-methoxyethoxymethyl azide (MEM-azide) [9]. Not unlike the addition of diazoalkane, the addition of an alkyl azide to C_{60} occurs across the [6,6] bond. At room temperature, the initially formed triazoline can be isolated in 35-40% yield. Thermolysis of the triazoline, followed by concomitant loss of nitrogen, gives rise to azafulleroids and fulleroaziridines. Fulleroaziridines and azafulleroids can also be obtained directly from C_{60} at higher reaction temperatures (160-180°C).

Interestingly, when azide addition reactions are carried out at temperatures ranging from 60-140°C, in addition to the formation of azafulleroid and fulleroaziridine a bisazafulleroid is formed and is the major product [4].



In an attempt to expand the scope of the chemoselectivity of the azafulleroid other cycloadditions were performed. Taking advantage of the fullerenes as sensitizers, we showed that self-sensitized photo-oxygenation of [60]N-MEM azafulleroid afforded the cage-opened [60]N-MEM ketolactam in high yield [5].



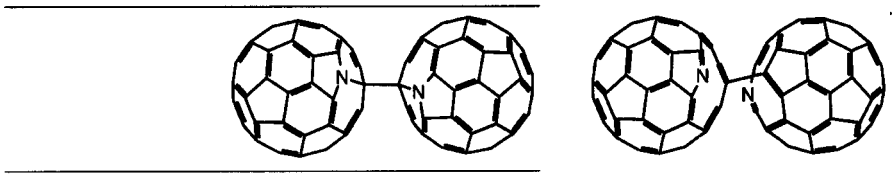
In the course of characterizing the ring-opened cluster, FAB mass spectroscopy revealed abase peak at *m/z* = 722. The exact mass of this ion, 721.9991, was consistent with molecular formula $C_{59}N^+$. Further confirmation was found in the 'shrink-wrap' [10] fragmentation pattern: loss of CN, *m/z* = 696 followed by the successive loss of C_2, *m/z* 672 and 648. Examination of the FAB mass fragmentation pattern of [60]N-MEM ketolactam to the azafulleronium $C_{59}N^+$ led us to propose the following mechanism (Scheme 1).

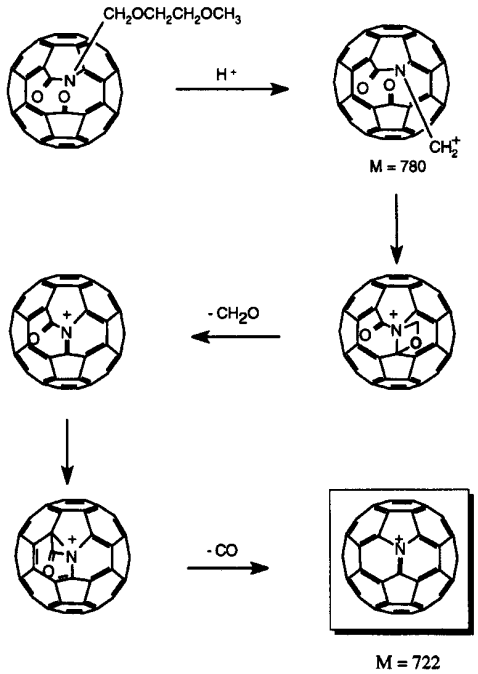
A relatively intense peak at *m/z* = 780 (95%) is due to loss of 2-methoxyethanol to yield the N-methyl carbonium ion, which is, in turn transformed to the four membered 1,3-oxazetidinium ring. The latter loses formaldehyde, followed by the loss of carbon monoxide to yield the azafulleronium ion.

We searched for a synthetic organic method that would mimic the events depicted previously to obtain macroscopic quantities of '$C_{59}N$'. A fast and remarkable reaction was observed when N-MEM ketolactam was treated with a large excess (15-20 equiv.) of pTsOH.H_20 in *ortho* dichlorobenzene (ODCB) at reflux temperature under an atmosphere of nitrogen [6]. The color of the reaction mixture changed from red-brown to green-brown upon formation of a non-polar major product. After purification by HPLC, the latter (green in solution) was shown by cyclic voltammetry, ^{13}C-NMR, FTIR, UV-vis, elemental analysis and mass spectrometry (electrospray) to be the azafullerene dimer $(C_{59}N)_2$.

A strong argument for the dimer was obtained from the cyclic voltammogram, which showed three pairs of reversible one-electron reductions. The appearance of closely-spaced pairs of waves in CV suggested that our system consisted of two (identical) weakly interacting electrophores. The ^{13}C-NMR spectrum of $(C_{59}N)_2$ showed 29 lines in the region between 157 and 124 ppm. Other resonances (i.e. sp^3 hybridized carbon atoms) were not observed.

We were forced by the ^{13}C-NMR results to conclude that the [6,6]-open structure is a possible structure of the azafullerene, because the [6,6]-closed structure has an sp^3 hybridized carbon atom, ordinarily expected to appear in the region of maximally 50-101 ppm.





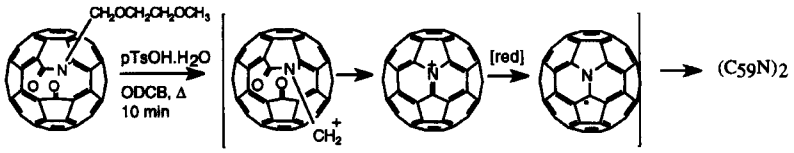
Scheme 1.

Having established its dimeric structure, we tried to rationalize this molecule's formation process. We proposed (Scheme 2) that the azafulleronium ion is formed first in a manner that mimics the gas-phase formation of azafulleronium, i.e. that the acid protonates the MEM moiety, inducing the loss of 2-methoxyethanol, followed by rearrangement to the azafulleronium ion. In the presence of the 2-methoxyethanol (or water) the azafulleronium ion can be reduced to the azafullerenyl radical. Finally, the radical dimerizes to yield $(C_{59}N)_2$.

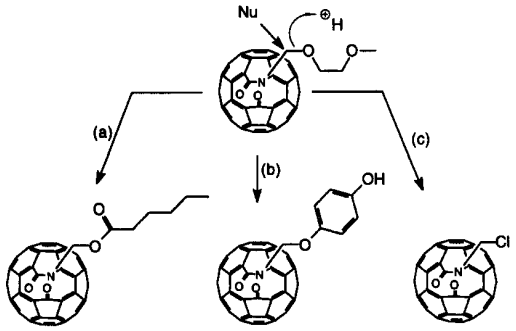
To corroborate the proposed mechanism for the formation of the azafullerene $(C_{59}N)_2$, we carried out the reaction in the presence of nucleophiles to trap the proposed carbonium ion intermediates [11]. This led to the isolation of new holey balls, fullerenes with a ring larger than a hexagon, as depicted in Scheme 3.

In the presence of excess p-toluenesolfonic acid monohydrate and hydroquinon, a stronger reducing agent than the 2-methoxy ethanol, in ODCB at 170-180°C, the ketolactam was converted to the desired hyroazafullerene as shown in Scheme 4 [11].

From the number of carbon resonances in the sp^2



Scheme 2.



(a) pTsOH H_2O, Hexanoic acid, ODCB, 180 C, 35%

(b) pTsOH H_2O, Hydroquinone, ODCB, 180 C, 50%

(c) $TiCl_4$, CH_2Cl_2, ODCB, 25 C, 47%

Scheme 3.

region (28) and a signal in the sp3 region (72.1 ppm), the hydroazafullerene was assigned to the closed structure with C_8 symmetry, as shown below.

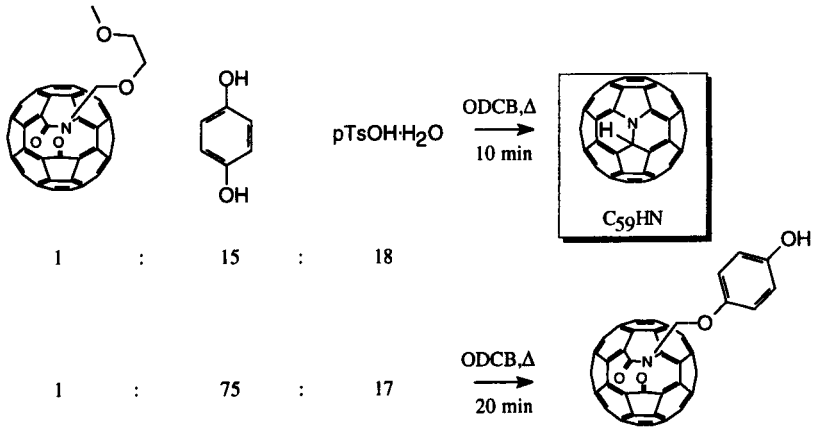
Azafullerene $C_{59}HN$ is green in common solvents and its UV-VIS spectrum is virtually identical to that of $(C_{59}N)_2$. Because the electronic absorption of $C_{59}HN$ and $(C_{59}N)_2$ are the same and the NMR data confirms the closed structure for $C_{59}HN$, the closed-closed structure was also assigned to $(C_{59}N)_2$ as well; even though, as

previously stated, the ^{13}C NMR of the latter does not show a signal in the sp^3 region.

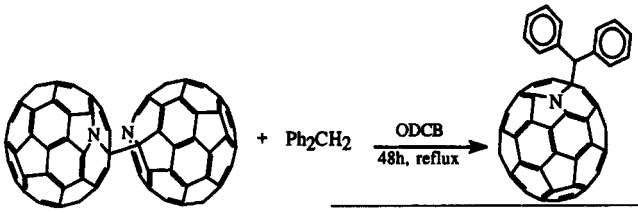
As part of our continued interest in the azafullerenes, we have initiated studies to prepare derivatives [8]. A principal reason for derivatization of $C_{59}N$ was to glean information on the variability of the chemical shift of the sp^3 carbon atoms as a function of substitution.

According to theoretical calculations [12] the inter-dimer bond of $(C_{59}N)_2$ is relatively weak (18 kcal/mol) and should, under photolysis or thermolysis conditions, undergo facile homolysis. We achieved derivatization of $C_{59}N$ by thermolytic dissociation of the inter-dimer bond of $(C_{59}N)_2$, followed by free radical reaction with a good hydrogen atom donor, diphenylmethane.

Treatment of $(C_{59}N)_2$ with excess diphenylmethane in refluxing ODCB for 48 h afforded, upon chromatographic purification, one product. This was shown to be the substituted azafullerene $C_{59}(CHPh_2)N$ by ^1H and ^{13}C NMR, FTIR, UV-vis, mass spectrometry, and cyclic voltammetry. The heterofullerene was obtained in 42% isolated yield after HPLC purification, demonstrating the

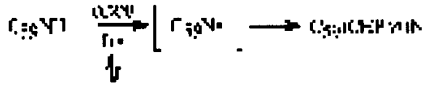


Scheme 4.



relatively clean conversion of $(C_{59}N)_2$ to a stable soluble derivative in cood yield (4).

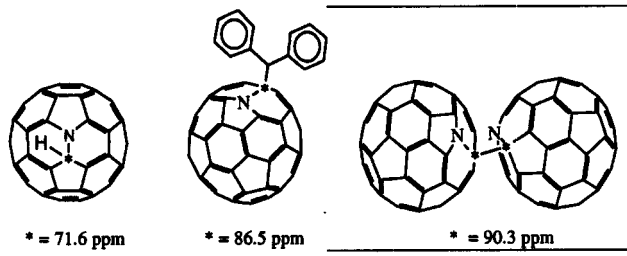
In the course of the reaction, formation of $C_{59}HN$ was



(5)

expected to be a dominant feature, however it was only 2% of the reaction mixture. A plausible explanation was that $C_{59}HN$, similar to $(C_{59}N)_2$, undergoes a free radical reaction to afford $C_{59}N\bullet$ (equation 5, above).

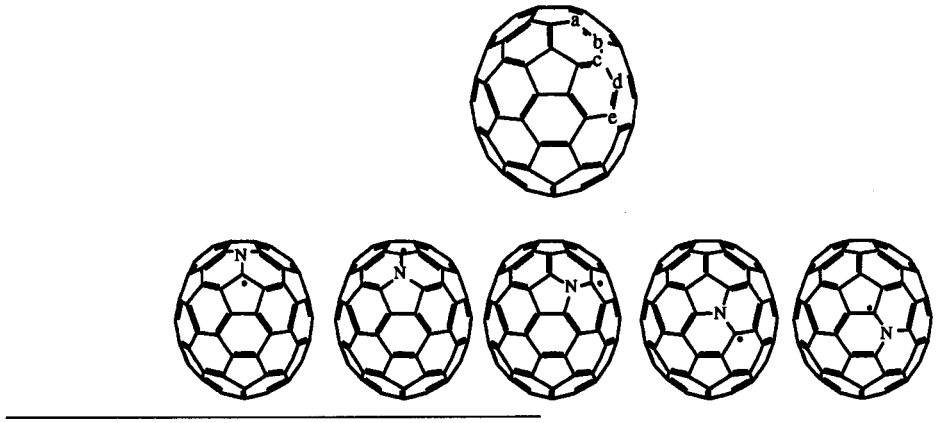
In a control experiment, treatment of $C_{59}HN$ with diphenylmethane in refluxing ODCB for 24 h, afforded, upon chromatography (silica gel, toluene) $C_{59}(CHPh_2)N$ in good yield as well as trace amounts of$(C_{59}N)_2$ and unreacted $C_{59}HN$. This study shows that $C_{59}HN$ can also undergo homolytic cleavage to yield the $C_{59}N$ radical,



where all three species $C_{59}N\bullet$, $C_{59}HN$ and $(C_{59}N)_2$ are involved in the process leading to $C_{59}RN$.

Full characterization of the adduct showed remarkable similarities to $(C_{59}N)_2$ and $C_{59}HN$, in particular the UV-vis data demonstrated that the electronic structure of all three molecules is essentially identical. The ^{13}C NMR spectrum of $C_{59}(CHPh_2)N$ revealed a similar pattern in the sp^2 region to that of its precursors and an unmistakable sp^3 carbon at 86.1 ppm, in agreement with a 'closed' structure. This carbon resonance is down-field shifted by 14 ppm relative to the sp^3 carbon of $C_{59}HN$ [11], as expected on going from hydrogen to alkyl substitution. ^{15}N NMR studies done on these compounds allowed assignment *a* of carbons *b*, to the nitrogen atom [13]. After, optimization for a long T_1, the ^{13}C NMR of $(C_{59}N)_2$ revealed an sp^3 carbon resonance at 90.3 ppm, corresponding to its inter-dimer carbon. This finally confirmed the closed structure as depicted below and illustrated the expected increase in chemical shift with increasing electronegativity of the substituent on the sp^3 center.

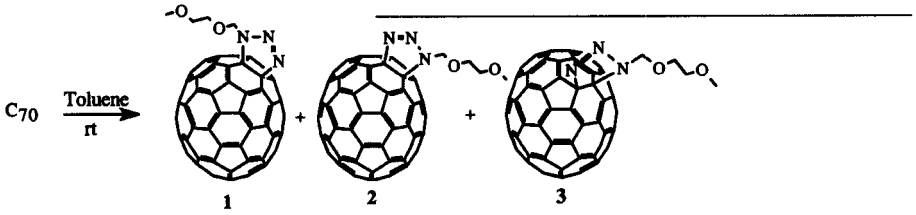
In an attempt to expand the scope of the heterofullerene family, we initiated similar studies with C_{70} [7]. Unlike



the transformation of C_{60} (I_h) to $C_{59}N$, C_{70} (D_{5h}) with its five different types of carbon atoms (see 'a'-'e' above) could, following the same strategy as describe previously, give rise to five distinct $C_{69}N\bullet$ isomers.

Simultaneous formation of all five radicals could lead to the formation of up to 15 different $C_{69}N$ dimers! With the synthesis outlined before for the formation of [60]azafullerenes and a solid understanding of the mechanism of formation we sought a selective synthesis of $(C_{69}N)_2$ isomers [14].

Similar to C_{60}, cycloaddition to C_{70} occurs across the [6,6] bond [7, 15-19] giving rise to a minimum of four possible isomers. The 1,3-dipolar addition of azide could, in principle, give rise to a maximum of six triazoline isomers, where addition across a [6,6] bond between two different types of carbon atoms gives rise to a pair of regioisomers, as depicted in Scheme 5 [15, 20].



At moderate temperatures the addition of MEM-azide to C_{70} gives rise to three triazoline isomers, where addition occurs to a greater extent across the [a,b] bond, the bond with greatest curvature, with preferential formation of **1**. Addition across the lower strain [c,c] bond also occurs but to a lesser extent, producing **3** (6).

In accord with theory [21], structures C_1(d,e), C_1(c,e) and C_s(e,e) (Scheme 5) are not observed. Also, by the same principle, azafulleroid **8** (below) is not observed. At 55°C triazoline **3**, a chemoisomer of regioisomers **1** and **2**, was readily and selectively transformed to azafulleroid **6** and aziridine **7** as well as a small quantity of C_{70}, whereas **1** and **2** remained intact, showing the varied stability of the isomers.

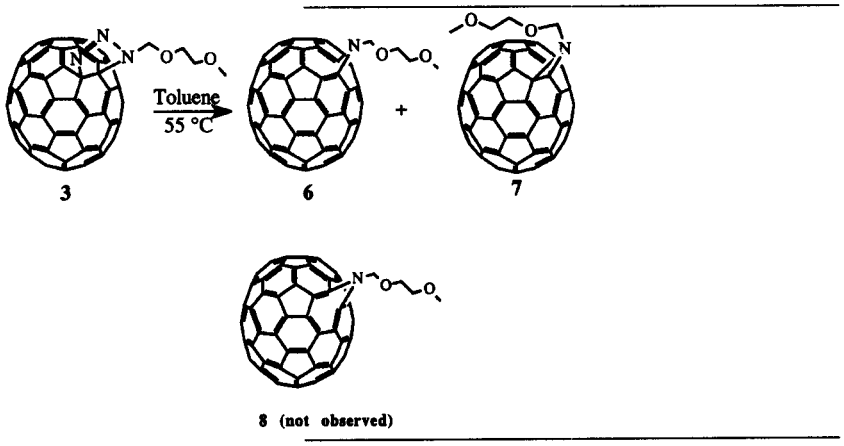
In comparing the thermal stability of **1**, **2** and **3**; the reduced stability of **3** is very likely due to the higher strain in its polar region; i.e. **1** and **2**, have a lower total strain energy than **3** because in the former, two of the polar carbon atoms are pyramidal and introduction of sp^3 carbons in the poles is expected to alleviate some of the polar strain of the C_{70} cluster.

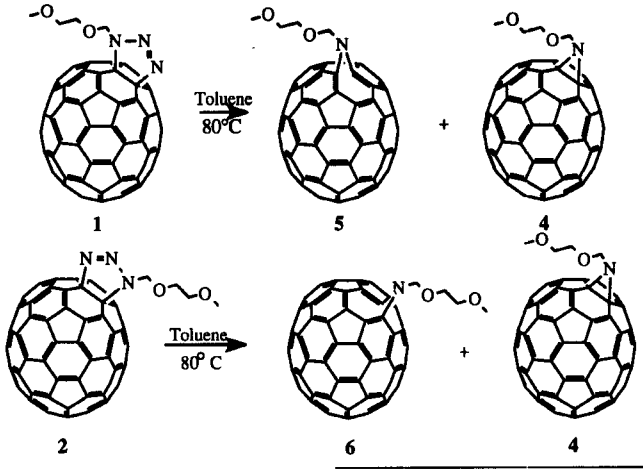
After separation of **1** and **2** by preparative HPLC, each was subjected to thermolysis. A dilute toluene solution of each isomer was heated to 80°C until the disappearance of the triazoline was observed by TLC [(8) and (9)]. In each case **1** or **2** gave rise to three separable bands by column chromatography (silica gel, toluene): C_{70} (64%), azafullerold **5** or **6** (23%), respectively, and aziridine **4** (5%).

When MEM-azide addition was carried out at a higher temperature (180°C), the preference of addition across the bond containing the greatest local curvature (a-b) (reflected in formation of **4**), as opposed to addition across the bond with the shortest bond order (c-c) (reflected in formation of **7**), decreased from 4:1 to 3:2.

This result reflects that: (1) at this temperature the MEM-azide also decomposes to MEM-nitrene which is expected to exhibit lower selectivity due its higher energy content; and (2) at a more elevated temperature the selectivity of the 1,3-dipolar addition is also expected to decrease. This study was the first step towards a full understanding of addition of azide to C_{70} and allowed for easy characterization of the subsequent transformation to azafulleroids. The addition of MEM-azide to C_{70} showed a wider range of selectivity than previously reported reactions of C_{70} such as osmylation [18] and addition of diazomethane [15].

Once we had a handle on the structures of the two [70] azafulleroids, we subjected each to photo-oxygenation.

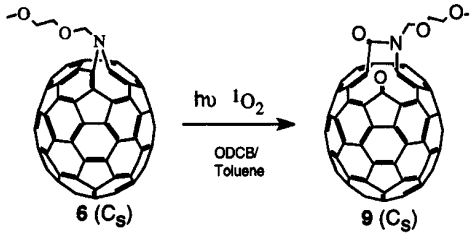




1 5 4

2 6 4

We first investigated the cage opening transformation of azafulleroid **6**. Due to its C_s symmetry, **6** afforded a single



6 (C_S) 9 (C_S)

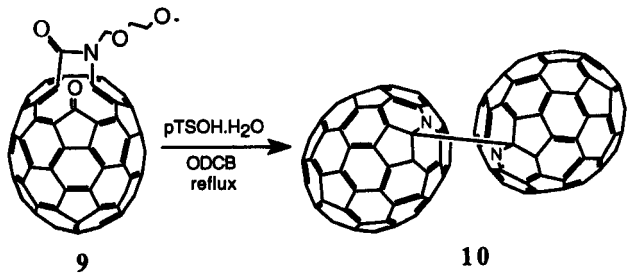
ketolactam isomer **9** upon a 2 + 2 addition of singlet oxygen, followed by decomposition of the 1,2-dioxetane intermediate. The structure of **9** was determined by FTIR, NMR and mass spectroscopy.

Similar to its [60]analog, the FAB mass spectrum of **9** revealed a base peak at *m/z* = 842, consistent with $C_{69}N^+$ [22]. Examination of the conversion of **9** to $C_{69}N$ suggests that only one $C_{69}N$ isomer should be formed, the [70]azafullerene where carbon 'a' is replaced by the nitrogen atom (Scheme 6).

going from C_{60} to $(C_{59}N)_2$ the retention time increases from 7 to 15 min. It is reasonable that the conversion of C_{70} to $(C_{69}N)_2$ would increase the retention time from 15 to 34 min. Electrospray analysis confirmed this, showing a molecular ion at *m/z* = 1685 and a strong base peak at *m/z* = 842. The ^{13}C NMR revealed 29 peaks in the sp^2 region, illustrating the high symmetry of the isomer. Due to the low solubility of the dimer and the tendency for sp^3 carbons adjacent to nitrogen to have long T_1 times, no resonances in the sp^3 region were found above the noise level.

Unlike **6**, azafulleroid **7** has C_1 symmetry, where photooxygenation could occur across the [a,b] bond or the [c,c] bond giving rise to two distinctly different ketolactam isomers. HPLC and ^1H NMR revealed the presence of two isomers in 4:1 ratio, both with C_1 symmetry. As we and other groups have demonstrated, addition reactions to C_{70} (at moderate temperatures) occur preferably across the [a,b] bond; designating **11** as the major product (Scheme 7).

Analysis of the decomposition of the ketolactam isomers **11** and **12** is shown below. In both cases the

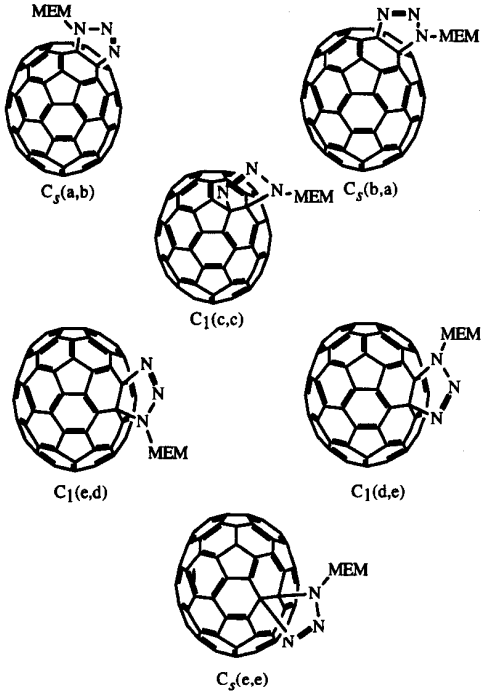


9 10

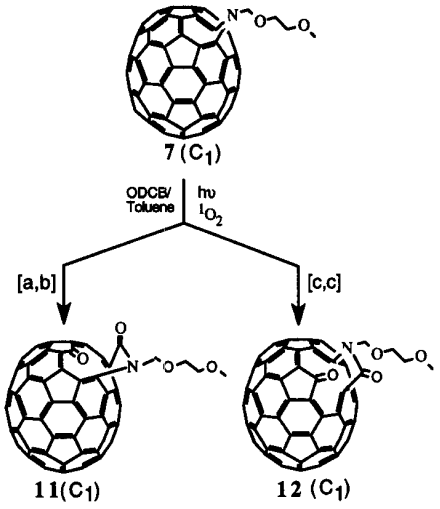
The stage was now set to chemically generate $C_{69}N$. Treatment of ketolactam **9** with an excess of pTsOH in refluxing ODCB produced a single apolar product **10** [19] as determined by HPLC; retention time 34 min (11).

This observation suggested that we had isolated the $C_{69}N$ as its dimer. This is based on the premises that on

mechanism suggests that each ketolactam isomer should give rise to a different $(C_{69}N)_2$ isomer; where decomposition of **11** leads to the exchange of carbon 'b' for nitrogen (Scheme 8(a)) and decomposition of **12** leads to exchange of carbon 'c' (Scheme 8(b)). Interestingly, the symmetry of **13** and **14** are different, allowing for the



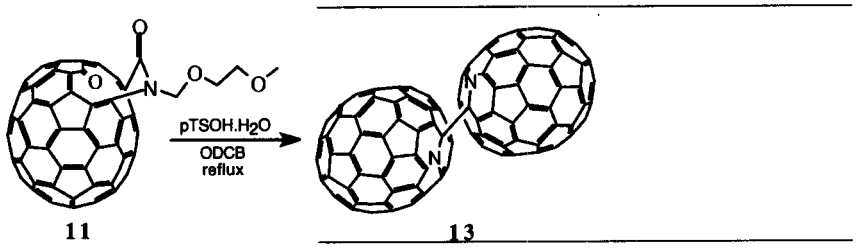
Scheme 5.



Scheme 7.

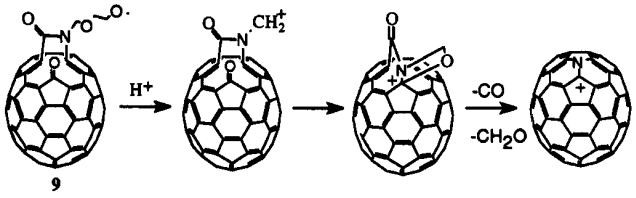
distinction of the two dimers as well as their ketolactam precursors.

After isolation and complete characterization of **11**, we subjected it to the acidic conditions described above for the conversion to $(C_{69}N)_2$. The electronic spectrum of the apolar product, after separation from pTsOH, was very similar to $(C_{69}N)_2$ isomer **10**; however HPLC revealed a single peak with a retention time of 41 min, 7 min longer than **10**.

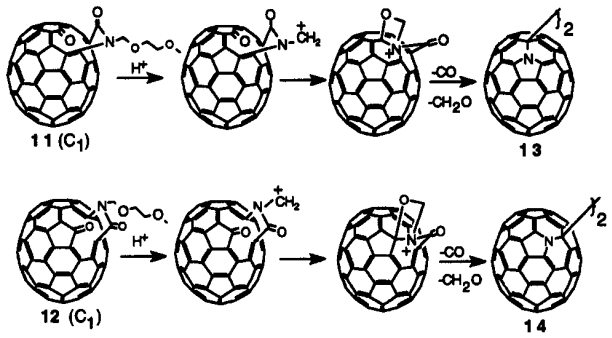


^{13}C NMR of **13** was also similar to that of **10** revealing ~30 carbon resonances in the sp^2 region. Efforts to prepare and fully characterize **14** are in progress.

In this paper we have reviewed the three step synthesis for the conversion of C_{60} to its heterofullerene analog $C_{59}N$. Postulation of a series of transformations in the gas phase leading to the formation of $C_{59}N^{(+)}$ was the basis for experiments that led to the synthesis of bulk quantities of the azafullerene dimer. Not unexpectedly, the intercluster bond of the dimer is relatively weak (18 kcal/mol) [12] and ready for homolysis which led us to exploit a homolytic approach to achieve derivation of the azafullerene cage by a free radical process. The ease of synthetic incorporation of a nitrogen atom into the fullerene skeleton had another important consequence; it provided the tool necessary to correctly assign the chemical shift of carbon atoms *a* and *b* to the heteroatom in $(C_{59}N)_2$, $C_{59}HN$ and $C_{59}(CHPh_2)N$ through a combination of ^{13}C NMR and ^{15}N-coupled ^{13}C NMR spectroscopy. Finally, realization that a fullerene sp^3 carbon atom bonded to nitrogen can have its T_1 relaxation



Scheme 6.



Scheme 8.

changed drastically was a key observation to help locate the missing inter-cluster carbon atoms at 90.3 ppm. This provided unequivocal proof that $(C_{50}N)_2$ has a [6,6]closed structure.

Lastly, we were very pleased to discover that the above methodology is applicable to the conversion of C_{70} to $C_{69}N$ and found that three out of the five possible $C_{69}N$ dimers can be formed selectively from their corresponding holey balls. In conclusion, we have discovered a general synthesis of azafullerenes which can be summarized as:

FULLERENE → AZAFULLEROID

→ HOLEY BALL → AZAFULLERENE

Acknowledgements - We thank the National Science Foundation for support through the Materials Research Science and Engineering Center as well as individual investigator grant DMR-9500888. Rosario González thanks the Ministerio de Educación y Ciencia (Spain) for a postdoctoral fellowship.

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